THE ROLE OF HYDROMETALLURGY IN THE RECYCLING OF ZINC, COPPER AND LEAD

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ÚLOHA HYDROMETALURGIE V RECYKLÁCII ZINKU, MEDI A OLOVA

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Abstrakt

Recyklácia kovov ostáva významnou industriálnou aktivitou a to tak z ekonomických ako aj environmentálnych dôvodov. V tomto prispevku je diskutovaná úloha hydrometalurgie pri recyklácii zinku, medi a olova. Boli vyvinuté hydrometalurgické procesy na odlúhovanie zinku z galvanicky pokoveného šrotu pred tavením, a takisto alkalické ako aj kyslé lúhovacie techniky za účelom odstránenia zinku z prachu pochádzajúceho z elektrických oblúkových pecí pred jeho recykláciou. Vysoké obsahy halogenidov v prachoch nasvedčujú, že procesy ako EZIMEX alebo Terra Gaia založené na chloridových systémoch môžu byť obzvlášť vhodné pre tento typ materiálov. Väčšina medeného šrotu je pretavená, ohňovo rafinovaná a odlievaná do anód pre elektrorafináciu. Pochopenie chovania sa rôznorodých nečistôt prítomných v medených anódach pripravených zo sekundárnych materiálov a ich riadený prechod do anódového kalu tvoriaceho sa počas elektrorafinácie sú kritickým parametrom pri výrobe vysokokvalitnej katódovej medi. Hydrometalurgia hrá významnú úlohu pri spracovaní kalu pochádzajúceho z použitých olovených akumulátorov; karbonátové lúhovanie je široko používané pri eliminácii sulfátovej frakcie kalu, čím sa podarí vyhnúť emisii SO_2 pri následnom pretavovaní olova. Úloha hydrometalurgie môže byť ďalej rozšírená, ak sa podarí vyvinúť stabilné anódy umožňujúce komerčnú implementáciu mnohých vyvíjaných elektrolúhovacích procesov pre spracovanie kalu z olovených akumulátorov.

Abstract

Metals recycling remains an important industrial activity for both economic and environmental reasons, and the role of hydrometallurgical processing in the recycling of zinc, copper and lead is discussed. Hydrometallurgical processes are being developed to leach zinc from galvanized steel scrap prior to remelting, and both alkaline and acid leaching technologies are being evaluated to eliminate zinc from electric arc furnace (EAF) dusts prior to their recycle. The high halogen content of the dusts, however, suggests that chloride-based systems, such as the EZINEX or Terra Gaia processes, could be especially useful for this material. Most copper scrap is melted, fire refined and cast into anodes for electrorefining. An understanding of the behaviour of the diverse impurities present in secondary copper anodes and their controlled rejection to the anode slimes generated during electrorefining are critical to the production of high quality cathode copper.

Hydrometallurgy plays an important role in the treatment of the paste component of spent lead-acid batteries: a carbonate leach is widely used to eliminate the sulphate fraction of the paste, thereby avoiding SO_2 gas emissions in subsequent smelting operations. The role of hydrometallurgy could be expanded if stable anodes could be developed to allow commercial implementation of the many leach-electrowinning processes under development for lead-acid battery paste.

Introduction

Metals such as iron, copper and lead have been produced since antiquity, and because of their high inherent value, they have always been extensively recycled. The early recycling practices were based on pyrometallurgical techniques, such as re-forging and remelting, to try to realize the maximum value from the metal which was produced initially at a very high relative cost because of the low productivity of the manual labour used. The modern age has seen the greatly expanded production of the traditional metals and the growth of new metals such as nickel, aluminum and magnesium. The relative value of all metals has decreased dramatically because of mechanized production methods; in some instances, metals have become a „throw-away" commodity, a situation which would have been unthinkable even a century ago. Despite the significant decline in the relative value of metals, their recycling remains an important aspect of modern society. Although metals recycling is often carried out for economic reasons, increasingly, recycling is done because of environmental or hygiene considerations.

Table 1 lists five tonnage metals and their 1995 production levels. Iron/steel is by far the most common metal in modern society, and its annual output greatly exceeds that of all other metals combined. Aluminum, copper, zinc and lead are the most commonly produced non-ferrous metals; their combined output exceeds that of the other non-ferrous metals. For example, the production of nickel is about 900,000 t/y, and that of magnesium, a growth metal, is only about 250,000 t/y. Hence, from a recycling point of view, the behaviour of the five metals shown in Table 1 is of paramount importance. The deportment of other metals, like cadmium or nickel, may have important ramifications from a hygiene or toxicological perspective, but they are of minor importance with respect to the overall tonnage of metals recycled.

Table 1 Annual production of five major metals

Metal	Production (t/y)
Iron/steel	700,000,000
Aluminum	20,000,000
Copper	12,000,000
Zinc	7,000,000
Lead	5,000,000

The metals listed in Table 1 are all recycled, and the relative contribution of recycled metal to total production ranges from ~60% for lead to ~15% for zinc. Despite the recent advances made in hydrometallurgy and the great selectivity of hydrometallurgical systems,

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most metal recycling is still based on pyrometallurgical techniques. For reactive metals such as aluminum, melting and molten metal refining are used to conserve the high energy content of the metallic phase. For less reactive metals like copper, smelting allows the collection and concentration of the metal in a form convenient for further refining. Nevertheless, hydrometallurgical techniques are important in the overall recycling of some metals, and this importance will likely increase as new technologies are developed. Within this framework, this paper discusses the role of hydrometallurgy in the recycling of zinc, copper and lead; it also presents some recent experimental work focused on the use of hydrometallurgy in the overall recycling of these metals.

THE RECYCLING OF ZINC, COPPER AND LEAD

Zinc-bearing Steel Plant Dusts

Although several thousand tonnes of scrap steel are used annually for cementation reactions or the generation of iron salts for water treatment, most iron and steel is simply remelted, commonly in electric arc furnaces (EAF) or in basic oxygen furnaces (BOF). The presence of galvanized steel in the scrap results in process dusts which are zinc-bearing and cannot, therefore, be recycled within the steel plant. There are two general approaches to overcome the problems caused by the presence of zinc. The first attempts to remove zinc from the steel scrap before it is melted, whereas the second, and more common method, is to eliminate the zinc from the dust prior to its recycle.

Early work on the removal of zinc coatings from scrap steel focused on sulphuric acid leaching [1]. Significant zinc recoveries, however, were realized only at low pH's where extensive iron dissolution also occurred. More promising is the use of sodium hydroxide solutions which readily dissolve zinc, lead and aluminum while leaving the steel largely unaffected. This option is being tested in a 48,000 t/y pilot plant operated by Metal Recovery Industries (MRI) [2]. The process was originally based on the anodically accelerated leaching of either 730 kg scrap bundles or shredded scrap. The published data suggest that the electrical energy requirements and the residence times increase as the size of the bundles increases. The process is more effective on shredded scrap, and presently, no anodic current is applied when loose shredded scrap is leached. Figure 1 shows the various processing steps, and it is important to recognize that a simple rotary drum is now used for the caustic leaching operation. The leaching process is carried out for ~2 h at 85°C in 5-10 M NaOH solution to remove up to 99% of the contained zinc. The de-zinced scrap is washed, and the washed scrap typically contains 0.01-0.02% Zn and 0.001-0.05% Na. It is readily recyclable within the steel industry. The sodium zincate solution is purified with zinc dust to remove Fe, Pb, Cu and Ni and is then electrowon with a current efficiency of ~90%. The zinc is produced as a fine dendritic powder [3] which can be melted under a suitable flux with a melting loss of about 10%. Various direct applications of the particulate zinc are being explored. The cost of the process is estimated at ~U.S. $35/t steel treated, when a credit for the by-product zinc is included. The cost is significant, however, when the low Zn content of the steel is considered, and of course, elimination of the zinc does not eliminate the EAF or BOF dusts, but only alters their compositions.

A more common approach is to treat the steel plant dust itself, and in this regard, Table 2 presents the range of compositions of the 1,400,000 t of EAF dust which are generated annually in the steel industry [4]. The EAF dusts are treated commercially by

pyrometallurgical methods such as waelz kilns, electrothermic furnaces, Imperial Smelting furnaces or flame reactors. Several plasma-based processes have also been applied to EAF dusts, but it is believed that all the plasma-based processes have ceased operation because of technical problems and high costs. All the pyrometallurgical options yield a leady ZnO product rich in halogens. Because of its impurity content, the ZnO has not yet found direct application in the primary zinc industry where its neutralizing capabilities would be an obvious benefit.

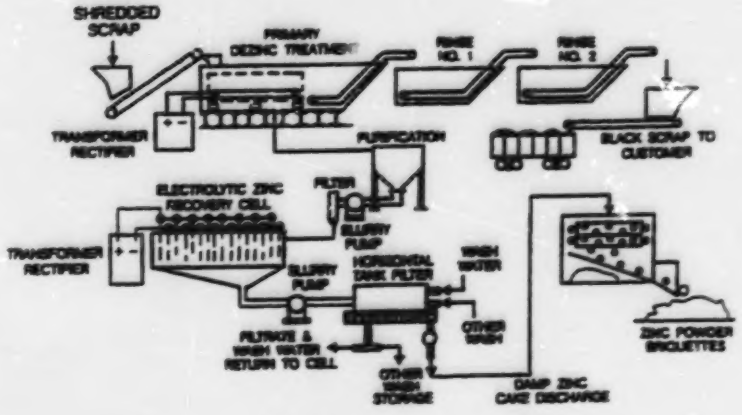

Fig.1 Schematic flowsheet of the MRI process for steel scrap (Ref.2)

Table 2 Compositional range of EAF dust (wt %)

Element	Compositional Range
Fe	20-40
Zn	10-30
Pb	1-4
Cl	0.5-3
F	0.1-0.5
Cu	0.1-0.3
Cd	0.02-0.1

A number of hydrometallurgical processes have also been developed to treat steel plant dusts. Early efforts were directed towards conventional H_2SO_4-based technologies. Those processes failed because of the high Fe/Zn ratio of the EAF dusts, and especially because of the high halogen content which cannot be accommodated during zinc sulphate electrolysis. Alkaline leaching offers the potential advantage that iron remains largely insoluble, and efforts to develop alkaline leaching technologies for EAF dusts continue. Such processes are limited, however, by their inability to recover zinc from zinc ferrite

unless a reducing roast is first carried out [5]. Both approaches result in halide-containing solutions, the processing of which is difficult. Because of the high chloride content of EAF dusts, chloride-based processing technologies could offer several advantages over H_2SO_4 or NaOH processing media. Hence, much of the recent hydrometallurgical activity related to the treatment of steel plant dusts has centered on chloride-based leaching systems.

The Zincex process [6,7] was originally developed to recover zinc from the chloride-sulphate solutions generated during the leaching of roasted pyrite ore. Those solutions contained about 2 M Cl and 20-30 g/L Zn which was present as various Zn-Cl complexes. The Zn-Cl complexes were extracted using a secondary amine, and the loaded organic was stripped with water to give an aqueous chloride solution containing Zn in the cationic form. The dissolved Zn was next extracted using DEHPA at pH 2.5, and the pH was kept constant by the addition of a lime slurry to the mixer-settlers. The loaded zinc was stripped with H_2SO_4 to yield a 90 g/L Zn sulphate solution suitable for conventional zinc electrolysis. As shown in Figure 2, the system effectively separates Zn from the chloride contaminant, but of course, creates a chloride solution which must be further processed prior to discharge.

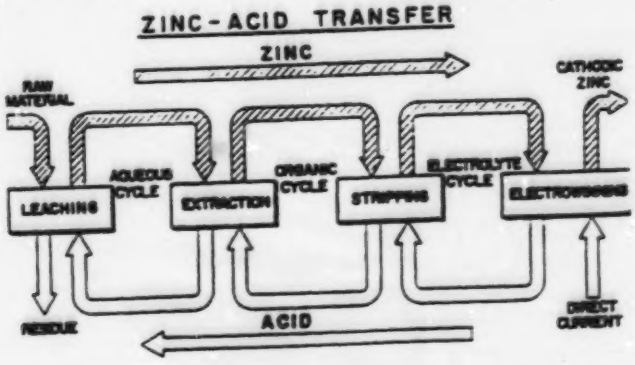

Fig 2 Use of the Zincex process to convert zinc from a chloride-containing solution to an all-sulphate medium (Ref 7).

As applied to EAF dust, the approach is to leach the dust in dilute sulphuric acid to solubilize the ZnO component which is then treated directly by DEPHA solvent extraction. The resulting leach residue can be treated by hot brine leaching to solubilize Pb and Ag prior to its recycle or discard. The final residue from the leaching of the EAF dust likely will contain some gypsum in addition to zinc ferrite. The presence of both Zn and SO_4 in the residue makes its recycle more difficult. The use of dilute HCL for the initial leach might simplify the overall flowsheet as applied to EAF dust.

A more recent development in the EZINEX process of Engitec Impianti [8,9] that is shown schematically in Figure 3. In this process, EAF dust is leached for 1 h at 70-80°C in an ammonium chloride-alkali chloride solution. The ZnO in the EAF dust is readily solubilized:

$$ZnO + 2NH_4Cl \rightarrow Zn(NH_3)_2Cl_2 + H_2O \qquad (1)$$

Although ZnO is readily dissolved. zinc ferrite is not appreciably attacked. After liquid-solids separation. the solution is treated with zinc dust to cement out Pb. Cu and Cd. The resulting solution typically contains 31-36 g/L Zn and <5 mg/L of Pb. Cu. Cd. Ni or Ag. The purified solution is finally electrolyzed according to the following equations:

$$Zn(NH_3)_2^{2+} + 2e^- \rightarrow Zn + 2NH_3 \quad (2)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (3)$$

$$Cl_2 + 2/3NH3 \rightarrow 2Cl^- + 2H^+ + 1/3N_2 \quad (4)$$

$$Zn(NH_3)_2Cl_2 + 2/3NH_3 \rightarrow Zn + 2NH_4Cl + 1/3N_2 \quad (5)$$

Hence. the chloride ion acts as a catalyst for the oxidation of ammonia to N_2 gas. The electrolysis cell operates at 200 A/m^2 and employs graphite anodes and titanium cathode plating blanks fitted with air spargers to enhance mass transport at the cathode. A compact. easily strippable Zn deposit is obtained.

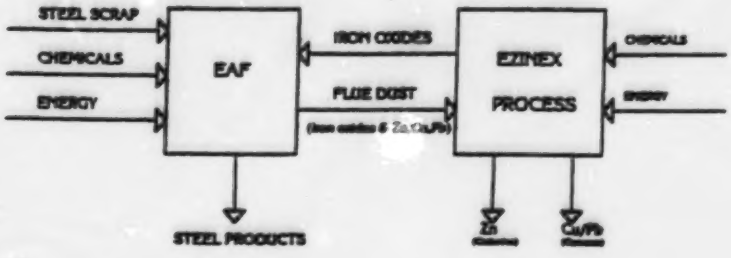

Fig.3 Use of the EZINEX process to treat EAF dust (Ref.8)

The leached EAF dust contains all the zinc ferrite which was originally present. This residue is mixed with coal and is dried prior to being recycled to the electric arc furnace. When the EAF dust was recycled at a rate of 1% of the furnace charge, all the Zn present in the ferrite was fumed. and about 70% of the recycled iron units were recovered in the molten steel. It is claimed that exhaustive recycling tests have been carried out at Ferriere Nord in Udine. Italy. and that no significant accumulation of impurities occurs in either the EAF dust or the steel. The implication is that the complete removal of all of the impurities in the leaching step is not required; it is only necessary to effect a significant bleed of Zn. Pb. Cu. etc. This is an important observation which could affect the development of other hydrometallurgical processes for EAF dusts. The EZINEX process requires only a small bleed of alkali and alkaline earth chloride salts. which can be recrystallized without a significant loss of the more soluble ammonium chloride. The EZINEX process has been extensively tested in a 500 t/y pilot plant facility and it is reported that a commercial plant is being installed at Ferriere Nord in Udine. Italy.

A somewhat similar process was developed by Hoogovens Ijmuiden and Delft University of Technology [10,11] for the treatment of zinc-bearing blast furnace dust. This product differs from EAF dust in that zinc ferrite is largely absent. In the proposed

process, shown schematically in Figure 4, the dust is leached under oxidizing conditions at 125-140°C in hydrochloric acid or in ferrous chloride-containing spent pickle liquor.

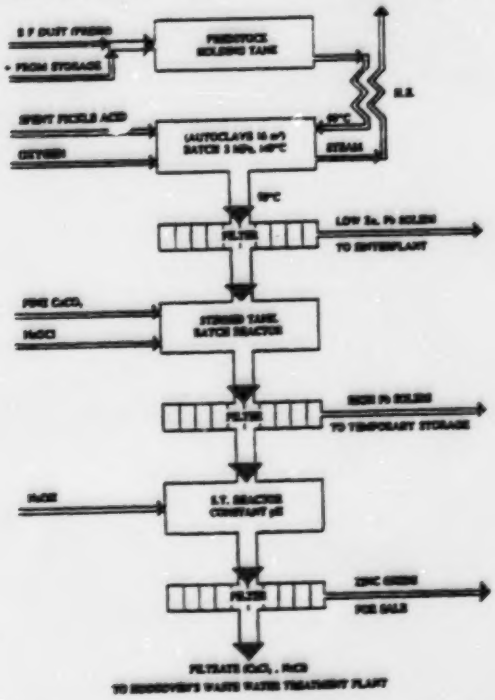

Fig.4 Chloride-based leaching system for the treatment of zinc-bearing blast furnace dust (Ref.11)

The zinc and lead are readily dissolved, but only minor iron leaching occurs. The limited amount of iron dissolution is achieved by controlling the solution pH to limit the attack of the iron oxides and by operating the leach autoclave at a sufficiently high O_2 pressure and temperature that iron oxidation-hydrolysis occurs. As was the case for the EZINEX process, the iron-rich residue is filtered and recycled to the steel plant. In this regard, it should be noted that the extractions of both Zn and Pb from the dust exceed 95%. The solubilized Pb is precipitated as an oxide by the addition of NaOCl and finely ground limestone. Next, chloride-free (<0.5% Cl) ZnO is precipitated by the addition of NaOH under carefully controlled conditions [12]; presumably the ZnO would be a readily marketable product. The remaining solution contains both $CaCl_2$ and NaCl; these salts are discarded after passage through a conventional water treatment facility. As a general observation, the recovery of potentially marketable Zn and Pb products and the recycle of the important iron units contained in the blast furnace dust are positive features of this type of hydrometallurgical process.

The Terra Gaia process is based on the dissolution of both ZnO and $ZnFe_2O_4$ in $FeCl_3$-HCl media at 175°C [13], as is illustrated in the flowsheet given in Figure 5. The

EAF dust is stirred with a ferrous chloride solution, made by reacting scrap iron with Cl_2 gas, and is then injected into an autoclave at 175°C. Oxygen is also injected with the result that the $FeCl_2$ is oxidized to $FeCl_3$ which hydrolyzes extensively at 175°C:

$$2FeCl_2 + 1/2O_2 + 2H_2O \rightarrow Fe_2O_3 + 4HCl \quad (6)$$

The generated hydrochloric acid attacks both the ZnO and $ZnFe_2O_4$ constituents, and any residual $FeCl_3$ reacts rapidly with the ZnO:

$$2FeCl_3 + 3ZnO + H_2O \rightarrow 2FeOOH + 3ZnCl_2 \quad (7)$$
$$2FeOOH \rightarrow Fe_2O_3 + H_2O \quad (8)$$

Presumably, the abundant Fe_2O_3 in the EAF dust passes through the autoclave largely unaffected. Preliminary test work has shown that Zn and Pb extractions consistently exceed 98% and that the resulting hematite residue can be recycled within a steel plant or safely discarded.

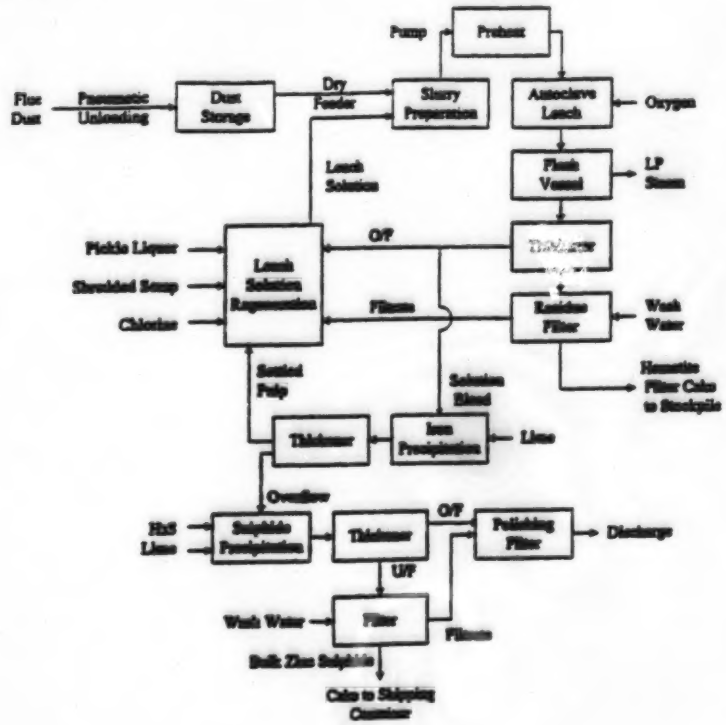

Fig.5 Schematic flowsheet of the Terra Gaia process for the treatment of EAF dust (Ref.13)

Recent fundamental studies done at CANMET [14] have helped to clarify the behaviour of $FeCl_3$ solutions at elevated temperatures. In this regard, Figure 6 shows the composition of the precipitates made at various temperatures when 0.3 M $FeCl_3$ solutions were heated for 3 h in the absence of hematite seed. At temperatures <115°C, akaganeite (β-FeOOH) is formed that has a low Fe content and a characteristically high Cl content. As the reaction temperature is raised, the Fe content of the precipitate rises while the Cl content falls, and this trend continues until ~140°C, whereafter nearly constant compositions are attained. The difference is a reflection of the precipitation of hematite rather than akaganeite. Significant is the observation that in the presence of hematite seed, the akaganeite-hematite transition can be displaced to temperatures as low as 100°C.

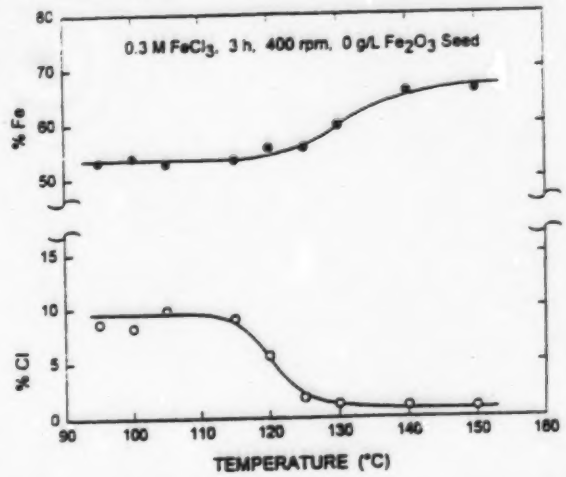

Fig.6 Effect of temperature on the composition of the iron precipitates made from $FeCl_3$ media

Figure 7 illustrates the effect of the initial addition of acid or base on the amount of hematite formed at 150°C in the presence of hematite seed. The „zero" point reflects the amount of precipitate made from a 0.4 M $FeCl_3$ solution to which neither acid nor base was added. Increasing acid concentrations adversely affect the precipitation of hematite and no net product formation occurred at 0.6 M HCl. The addition of base, on the other hand, increases the amount of hematite formed. These results show that the hematite precipitation reaction is readily reversible at 150°C:

$$2FeCl_3 + 3H_2O \Leftrightarrow Fe_2O_3 + 6HCl \qquad (9)$$

This is an important observation relative to the chloride leaching of EAF dusts at high temperatures because it means that the system is self-buffering with respect to acid concentration. If too much acid is present, some of the abundant hematite will dissolve to make $FeCl_3$. Conversely, if too little acid is present, $FeCl_3$ will hydrolyze to generate sufficient acid to allow the dissolution of additional ferrites present in the EAF dust.

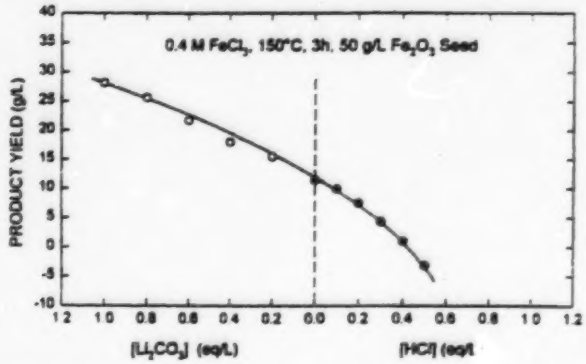

Fig.7 Effect of acid/base concentration on the amount of hematite precipitated from FeCl, media

The hematite made from chloride media incorporates a modest amount of Cl but only negligible amounts of Zn. For example, the precipitate made at 150 °C contains 67-68% Fe, ~0.2% Cl and only 0.03% Zn. It is believed that such material could be recycled without difficulty in a steel plant. Of course, the recovery of Zn and Pb from the processing solution would be required, and in the Terra Gaia process, it is proposed to precipitate these metals as sulphides. It is also proposed to discard the resulting brine, but clearly this practice is site-specific.

Hydrometallury in the Recycling of Copper

The hydrometallurgical treatment of copper ores and concentrates is highly developed and accounts for approximately 20% of the world's primary copper production. The key to the success of the hydrometallurgical route has been the development of solvent extraction reagents which can selectively recover Cu from dilute leach solutions. The loaded extractants are then stripped by sulphuric acid to yield a solution suitable for electrolysis to high purity metal. Other positive factors have been the extensive automation of the refineries to lower processing costs and a better understanding of the leaching reactions to maximize copper extractions. Several efforts have been made to extend this hydrometallurgical expertise to the recycling of copper metal, either by a leach-electrowinning approach or by direct electrorefining of scrap in „baskets". Generally, such efforts have not been economically successful. Despite the great success of hydrometallurgy in the primary copper industry, pyrometallurgy remains the dominant tool in the recycling of copper metal.

By way of illustration, Table 3 shows the ultimate destination of various types of copper scrap in North America. High grade scrap, consisting of almost pure copper metal, is used directly for the manufacture of brass and bronze. This material is simply melted and alloyed to the appropriate composition. Any impurities present can be tolerated within the specifications of the alloy, or are significantly diluted by blending. Slightly lower grade material is processed in copper refineries, where it is blended, melted and cast into anodes. Lower grade material is commonly processed in small shaft furnaces, with or

without a converting step. The resulting ingots of black copper can be fire refined or sold to copper smelters for addition to the converters as cold dope. Still lower grade material is commonly processed in copper smelters, and the cut-off copper grade is strongly dependent on the impurity or precious metal contents of the scrap. The important observation, however, is that all the copper is treated, at least initially, by pyrometallurgical methods to yield either a marketable product or anodes for electrorefining. When the scrap copper is processed in a primary smelter, it is so diluted that the anodes behave essentially like primary copper anodes. When the copper is processed in a secondary refinery, however, the resulting anodes are materially different, and their behaviour during aqueous electrorefining may be significantly different, from those cast in a primary smelter.

Table 3 Copper recycling in North America

Type of Recycler	Tonnage Treated	Typical Copper Content (wt %)
Brass Mills	600,000	99.8
Primary or Secondary		
Copper Refineries	430,000	96
Ingot Makers	270,000	70
Copper Smelters	250,000	25-35

The behaviour of various kinds of anodes during copper electrorefining is of relevance to the industry, and has been an on-going research activity at CANMET for a number of years. Although there are no secondary copper refineries in Canada, CANMET recently carried out detailed studies of the secondary anodes and anode slimes generated at the Copper Division of Southwire in the United States and at Huttenwerke Kaiser in Germany. Table 4 presents the compositions of two of the anodes studied. Relative to the anodes processed in primary operations, both anodes are notably deficient in Se, Te and Bi, and both contain only modest amounts of Ag. On the other hand, both anodes are notably enriched in Sn, Pb and Ni. Also, the oxygen content of the secondary anodes is higher than that of primary anodes. The difference may be attributable to the greater need to eliminate impurities during the fire refining of secondary copper.

Table 4 Compositions of two secondary copper anodes (wt %)

Element	Southwire	Huttenwerke Kaiser
Pb	0.068	0.18
Ni	0.125	0.36
Sb	0.018	0.05
Sn	0.040	0.01
Ag	0.025	0.03
As	0.038	0.07
Bi	0.002	—
Te	0.004	<0.001
Se	0.004	<0.01
O	0.273	0.23

Figure 8 illustrates the structure of the Southwire anode, and the anodes from Huttenwerke Kaiser are similar in their overall structure. The anode consists of individual copper crystals ~100 μm in size that are delineated by tiny bright- or dark-appearing grain boundary inclusions. The dark-appearing inclusions are Cu_2O, and there is more Cu_2O in the Southwire anode than would normally be encountered in an anode from a primary copper refinery. In particular, there is an abundance of the Cu-Cu_2O eutectic structure between the copper crystals. The implication is that secondary copper refineries may overblow the metal during fire refining to aid in the oxidation of impurities. Of course, the excess of Cu_2O creates copper balance problems in the tankhouse, but these problems are clearly not as critical as the need to reject impurities in the fire refining operation. The bright-appearing grains are either tin oxide or various Cu-Pb-As-Sb oxides.

Most of the bright appearing grains are SnO_2, and in some instances, these are present as well-formed crystals, as is evident in Figure 9. All of the brighter particles are crystals of SnO_2, which in many cases, exhibit relatively sharp external crystal faces suggesting that the SnO_2 crystallized in the molten copper. The abundance of tin oxide seems to be characteristic of secondary copper anodes.

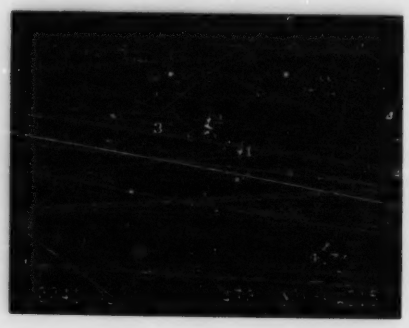

Fig.8 Backscattered electron micrograph showing the general appearance of the Southwire anode. 1-Cu_2O, 2-SnO_2, 3-copper, 4-Cu-Pb-As-Sb oxide

Fig.9 Backscattered electron micrograph illustrating the SnO_2 crystals in the Southwire anode. 1-SnO_2, 2-copper, 3-Cu_2O

Although about 40% of the total Pb content of the secondary anodes is in solid solution in the copper metal matrix, the remainder is present as complex oxide inclusions concentrated at the grain boundaries between the copper crystals. In this regard, Figure 10 shows a typical inclusion present in the Southwire anodes. The dark-appearing regions are Cu_2O and the medium grey areas are euhedral SnO_2 crystals. The bright-appearing phase, however, is Cu-Pb-As-Sb oxide, a compound which is abundant in the Southwire anodes and also occurs in the Huttenwerke Kaiser anodes. In this regard, Figure 11 illustrates a somewhat similar spheroidal inclusion present in the Huttenwerke Kaiser anodes. The bright-appearing phase is Cu-Pb-As-Sb oxide and the grey, bladed crystals are Cu-Ni-Sb oxide (Kupferglimmer); the black-apearing phase is Cu_2O. A number of Sn-Pb-Sb-As oxide phases were detected in the anodes in lesser amounts, and some of these phases have not been reported in the anodes from primary copper refineries. Of course, the copper

selenide-telluride inclusions which are a prominent feature of primary copper anodes and play a major role in the behaviour of silver are almost absent from all secondary anodes

Fig.10 Backscattered electron micrograph of a typical grain boundary inclusion in the Southwire anode. 1-copper, 2-Cu-Pb-As-Sb oxide,3-SnO_2, 4-Cu_2O

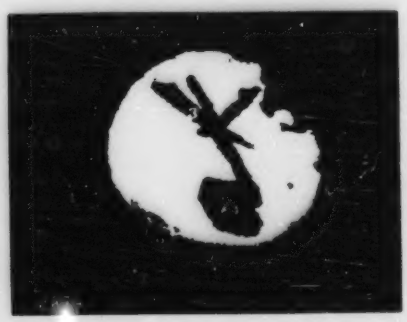

Fig.11 Backscattered electron micrograph showing a grain boundary inclusion in the Huttenwerke Kaiser anode. 1-copper, 2-Cu-Pb-As-Sb oxide, 3-Cu-Ni-Sb oxide (Kupferglimmer), 4-Cu_2O

The behaviour of the „different" suite of inclusions in the secondary anodes during electrorefining could impact significantly on both the electrolyte composition and the formation of suspended slimes. These factors, in turn, strongly influence the quality of the cathode deposits. Perhaps the major role of the hydrometallurgist in the secondary copper industry will be the elucidation of the behaviour of the diverse impurities during electrorefining and the development of strategies to minimize their impact on copper cathode quality [15,16].

With respect to the behaviour of impurities during the electrorefining of anodes made from recycled copper, mineralogical and chemical studies were also carried out on the anode slimes generated in both the Southwire and Huttenwerke Kaiser secondary refineries. Such studies define the species which accumulate in the anode slimes and also indicate possible reactions which could cause the dissolution of some phases and the precipitation of new compounds.

Figure 12 illustrates the anode slimes formed in the Southwire refinery, and Figure 13 shows the analogous product made at Huttenwerke Kaiser. Large well formed SnO_2 crystals are evident in both slimes samples, and the morphologies of the crystals are generally similar to those detected in the unrefined copper anodes. Furthermore, none of the SnO_2 crystals shows any evidence of partial dissolution or reaction with the electrolyte. One of the SnO_2 particles in the Huttenwerke Kaiser slimes is rimmed with Sb-Ni-Cu oxide, but such rims were also detected in the unrefined anodes processed in that plant. The implication is that the tin oxide is „inert" during electrorefining. It simply accumulates in the anode slimes, and is unlikely to affect the overall refining process. Lead sulphate is abundant in the slimes from both refineries, and in some instances, the $PbSO_4$ particles have the same morphology as the Cu-Pb-As-Sb oxide inclusions in the unrefined anode (cf. Figure 11). Presumably, the $PbSO_4$ forms by the acid attack of the

original Cu-Pb-As-Sb oxide phase that converts the lead to $PbSO_4$ and solubilizes most of the Cu. As and Sb. The $PbSO_4$ also accumulates in the anode slimes, and coarser particles of this phase probably do not affect cathode quality. Fine particles of $PbSO_4$, however, could be suspended in the electrolyte and could become trapped on rough areas of the cathode, thereby reducing the chemical purity of the copper product. The various fine particles in the anode slimes are often agglomerated into larger masses by an oxidate phase which contains major amounts of Cu, Ag, AsO_4 and SO_4 together with minor amounts of Pb and Sb. This type of material has been found in the anode slimes from several primary copper refineries, and it is believed to consist of an intimate mixture of Cu, Ag and Pb arsenates, sulphates and antimonates.

Fig.12 Backscattered electron micrograph showing the general appearance of the Southwire anode slimes. 1-SnO_2, 2-$PbSO_4$, 3-Pb-Sb oxide, 4-Sn-Ni-Zn-Fe oxide, 5-oxidate phase, 6-Ag

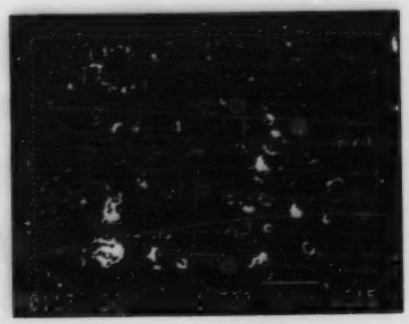

Fig.13 Backscattered electron micrograph illustrating the general appearance of the Huttenwerke Kaiser anode slimes. 1-SnO_2, 2-Cu-Ni-Sb oxide, 3-Ag, 4-$PbSO_4$, 5-Sn-Ni-Zn-Fe oxide, 6-Sn-Sb-Ni-Cu oxide, 7-oxidate phase

Although many of the phases present in the anode slimes appear to have simply accumulated as the copper anode dissolved away, other phases clearly precipitated in the slimes layer. These latter compounds are of significance as they could equally precipitate elsewhere in the refining cell: e.g., on the cathode surface. Figure 14 illustrates a large mass of $AsSbO_4$ in the Southwire anode slimes that is composed of small well formed individual crystals. Similar material was detected in the slimes from Huttenwerke Kaiser. Although trace amounts of Bi and Sn are sometimes detected, the phase is essentially $AsSbO_4$. The size and morphology of the $AsSbO_4$ particles indicate that they precipitated in the slimes layer; in other refineries, similar material has been reported to form on the walls of the refining cells. Precipitation of this phase on the cathode would adversely affect the purity of the copper deposit. Figure 15 illustrates the anode slimes from the Huttenwerke Kaiser refinery. Of note are the tiny dendritic particles of silver metal which occur as free grains or as larger masses agglomerated by the oxidate phase. The formation of fine dendritic silver seems to be characteristic of some secondary refining operations. In primary refineries, the silver either reacts with the copper selenide phase to form various Ag-Cu selenides or it forms compact grains on the surfaces of other particles [17]. The fine

silver dendrites illustrated in Figure 15 could easily become suspended in the electrolyte and might, therefore, be transferred to the cathode surface. It has been postulated that the presence of electrically conductive particles, like silver, on the cathode surface results in nodulation and reduced product purity.

Fig.14 Backscattered electron micrograph showing a large mass of $AsSbO_4$ in the Southwire slimes. 1-$AsSbO_4$, 2-SnO_2, 3-Ag,Se, 4-$PbSO_4$

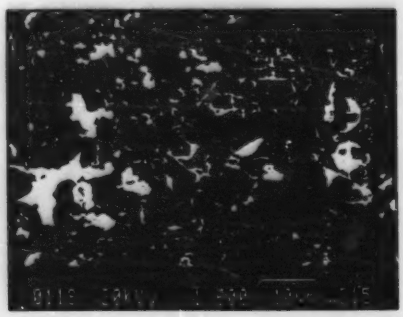

Fig.15 Backscattered electron micrograph showing the presence of Ag in the Huttenwerke Kaiser anode slimes. 1-$BaSO_4$, 2-$PbSO_4$, 3-Ag, 4-dentritic Ag, 5-Cu-Ag oxidate phase

It is likely that virtually all recycled copper metal will continue to be treated by pyrometallurgical techniques, and lower grade scrap will be melted, fire refined and cast into anodes for subsequent electrorefining. Accordingly, the critical role of the hydrometallurgist will be to ensure that the diverse impurities present in the secondary copper anodes remain in the anode slimes and that they do not contribute to cathode nodulation or reduced cathode purity.

Hydrometallury in the Recycling of Lead

Over 70% of the world's total output of lead is consumed in the manufacture of lead-acid storage batteries, most of which are used in the transportation industry. Growth in electric vehicle demand, coupled with restrictions on lead usage elsewhere, will likely result in an even greater fraction of the world's lead output being used for lead-acid batteries. Such batteries are readily collected and recycled and, as a result, they are the major feed to the large secondary lead industry. In fact, about half of the world's annual lead output originates from secondary sources; in the United States, over 70% of the total lead consumed is from secondary material, mostly lead-acid batteries. During the processing of the spent batteries, the lead-rich phases are isolated and concentrated by magnetic separation to remove tramp iron and by a series of classification and washing operations [18]. The battery grids contain >90% metallic lead and are readily remelted. The battery paste, however, is more complex and is known to contain $PbSO_4$ in addition to a number of other phases. To aid in the development of technologies to recycle lead-acid batteries, CANMET recently carried out a mineralogical study of the phases present in the battery paste from a Canadian secondary lead plant, and reference to that study is instructive [19].

The bulk chemical composition of the battery paste is given in Table 5. The battery paste consists mostly of Pb and SO_4 together with lesser amounts of Ca and Sb; significantly, the Pb/SO_4 ratio is greater than that of $PbSO_4$ and this suggests the presence of various Pb oxides and/or metallic lead.

Table 5 Chemical composition of typical lead-acid battery paste (wt %)

Element	Composition
Pb	71.2
SO_4	18.1
Sb	0.3
Ca	0.4
SiO_2	0.14
As	<0.04
Sn	<0.1

X-ray diffraction analysis of the battery paste indicated major amounts of $PbSO_4$ and PbO_2, together with minor quantities of $Pb_2O(SO_4)$ and Pb metal. More detailed SEM-EDX study of the battery paste confirmed the X-ray diffraction results and provided additional information on the other constituents present. In this regard, Figure 16 shows a large mass of $PbSO_4$ which contains numerous bright inclusions of Pb metal as well as patches of $Pb_2O(SO_4)$. Such large masses of $PbSO_4$ are abundant in the battery paste and comprise >50% of the mass of the sample. Lead dioxide (PbO_2) is often intergrown with $PbSO_4$ as is shown in Figure 17.

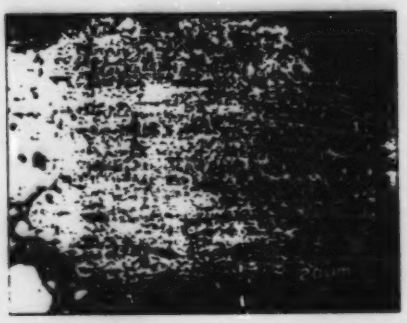

Fig.16 Backscattered electron micrograph of a $PbSO_4$ particle in the lead-acid battery paste 1-$PbSO_4$, 2-Pb, 3-$Pb_2O(SO_4)$

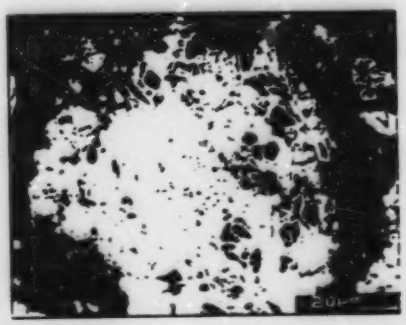

Fig.17 Backscattered electron micrograph showing an occurrence of PbO_2 in the battery paste 1-$Pb_2O(SO_4)$, 2-$PbSO_4$, 3-PbO_2

The core of the particle consists of $Pb_2O(SO_4)$ surrounded by coarse grained $PbSO_4$. The bright coating on the $PbSO_4$ is PbO_2. Although $Pb_2O(SO_4)$ often occurs as compact masses as illustrated in Figure 17, a more common occurrence is as intergrowths of fibrous crystals as is shown in Figure 18. The $Pb_2O(SO_4)$ phase is moderately abundant in the battery paste.

and its presence is important as it behaves differently than $PbSO_4$ in hydrometallurgical systems. Although not detected by X-ray diffraction methods, Pb_2O_3 is also moderately abundant in the battery paste, and the implication is that the Pb_2O_3 phase is poorly crystalline. Figure 19 shows a large mass of Pb_2O_3 which progressively grades into PbO_2, $PbSO_4$ and $Pb_2O(SO_4)$. As might be expected, the presence of sulphate-containing phases in the battery paste complicates the processing of this material by pyrometallurgical methods since extensive scrubbing systems are required to contain the relatively minor quantities of SO_2 gas evolved.

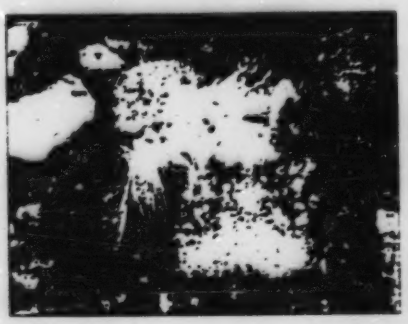

Fig.18 Backscattered electron micrograph of a cluster of $Pb_2O(SO_4)$ crystals in the battery paste. 1-$Pb_2O(SO_4)$, 2-$PbSO_4$, 3-Pb

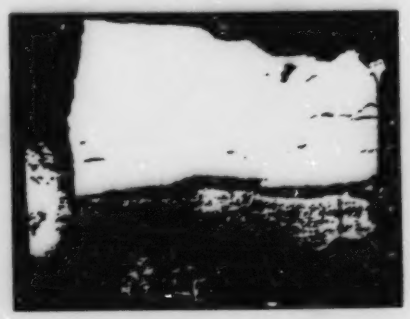

Fig.19 Backscattered electron micrograph of a banded oxide particle in the battery paste. 1-Pb_2O_3, 2-PbO_2, 3-Pb_2O_3, 3-$PbSO_4$, 4-$Pb_2O(SO_4)$

One solution to the environmental problems associated with the direct smelting of lead-acid battery paste is to leach the associated lead and subsequently recover it electrolytically [20]. Table 6 summarizes the more developed leach-electrowinning processes for lead-acid battery paste, and Figure 20 illustrates a schematic flowsheet of a typical process [21]. All the processes developed to-date face common problems associated with the elimination of sulphate from the system and with the dissolution of the lead oxides. Most processes eliminate $PbSO_4$ by reaction with sodium carbonate or ammonium carbonate solutions according to the following simplified reaction.

$$PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4 \qquad (10)$$

Although the indicated reaction proceeds very rapidly for $PbSO_4$ [22], it is much slower for $Pb_2O(SO_4)$, which is also present in the battery paste. Once the sulphate content of the battery paste has been eliminated, the resulting product is leached in a solution which has a high solubility for lead. For practical reasons, suitable leaching media are restricted to fluosilicic acid (H_2SiF_6), fluoboric acid (HBF_4), ammoniacal ammonium sulphate or concentrated chloride solutions. The former two systems offer the advantage that the lead is electrodeposited as a compact plate. The latter systems yield lead sponge or dendrites. A major problem exists with all the lixiviants in that, although lead carbonate is readily leached, PbO_2 and Pb_2O_3 require reduction to PbO prior to their dissolution.

Table 6 Leach-electrolysis processes for lead-acid batery

Technology	Paste Treatment	PbO_2 Control	Electrolyte	Anode
RSR process	ammonium carbonate leach	SO_2 reduction or reductive roast	H_2SiF_6 + H_3BO_3, AsO_4 addition	graphite covered with inert mesh coated with PbO_2
Bureau of Mines process	ammonium carbonate leach	Pb powder reduction	H_2SiF_6, PO_4 addition	PbO_2-coated titanium
M.A. Industries process	ammonium carbonate leach	redox couple	HBF_4	graphite
Engitec process	sodium carbonate-sodium hydroxide leach	Pb powder + H_2O_2	HBF_4	composite anode operating at high current density with H_2O_2 additions
AAS process	ammonical ammonium sulphate leach	residue leached in concentrated H_2SO_4 at 60°C	ammonical ammonium sulphate leach solution	
Ginatta process	ammonium carbonate leach	—	HBF_4	graphite with cobalt additives
PLACID process	HCl-NaCl leach	PbO_2 + Pb in HCl	HCl-NaCl brine	membrane cell-titanium DSA anodes

The electrowinning of lead is complicated by the formation of PbO_2 at the anode. Fortunately, the addition of ~1 g/L of As or P (as AsO_4 or PO_4) prevents the anodic deposition of PbO_2, and such additions are commonly incorporated in the electrolyte along with various reagents to promote smooth lead deposits. In contrast, lead electrowinning from concentrated chloride media does not result in the formation of PbO_2. The PLACID cell, shown schematically in Figure 21, claims to make O_2 at the anode [23], although the

evolution of Cl_2 gas is an ever-present danger. Electrolysis is typically carried out at a current density of 150-400 A/m^2 and with an energy requirement of <1 kWh/kg lead produced. In chloride media, current densities as high as 1.200 A/m2 are used. The lead deposit typically contains 99.99% Pb. Although the purity of the electrodeposit is high, it is often inadequate for the direct production of battery grids and must be further refined by pyrometallurgical methods.

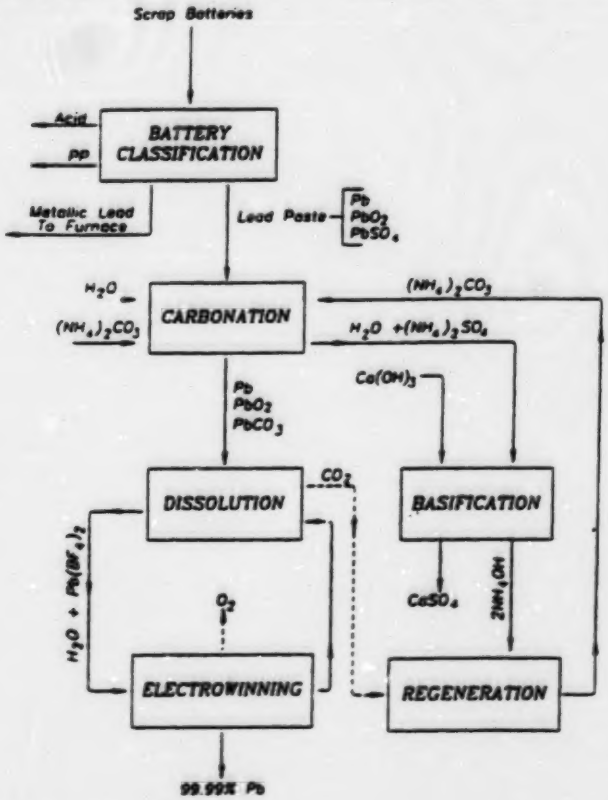

Fig.20 Typical flowsheet for the electrolytic recovery of lead from lead-acid battery paste (Ref.21)

The above discussion and Table 6 indicate that the dissolution of battery paste in a suitable lixiviant, followed by the electrolytic recovery of lead metal from the solution is an attractive processing option. Although the leaching part of the process is not without problems, various process modifications have been made to address all the concerns. Lead electrolysis can proceed without the formation of PbO_2 at the anode, and in many systems, compact lead deposits are produced. A major difficulty with all the electrolytic processes, however, is the life of the anodes. Sophisticated anodes are required to evolve O_2 gas from highly corrosive fluoride-containing media. A number of anode materials have been identified that perform satisfactorily in short term pilot plant campaigns. None of the

anodes, however, seems capable of providing industrially acceptable anode longevity (i.e., ~2 y) [24]. The problem is not as critical in concentrated chloride media, however, and titanium mesh-DSA anodes may be suitable for chloride-based electrowinning cells [23]. Clearly, the critical need in the leach-electrowin approach for lead-acid battery paste is the development of an O_2-evolving anode having significant longevity in fluoride-containing electrolytes.

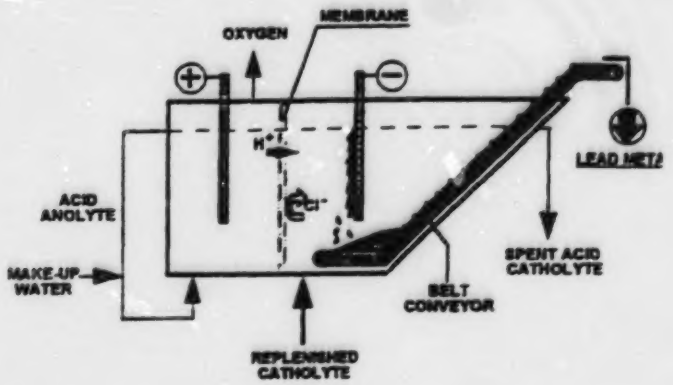

Fig.21 Schematic representation of the PLACID lead electrowinning cell (Ref.23)

Another option for the treatment of lead-acid battery paste is to react the paste with sodium carbonate solution to eliminate the sulphate and then to smelt the product in the presence of a reducing agent. A typical flowsheet of this option is given in Figure 22. There are many variations to this processing approach, but a common unit operation in all the technologies is the hydrometallurgical conversion of the lead sulphates to carbonates, thereby avoiding the evolution of low-concentration SO_2 gases during smelting. The conversion of $PbSO_4$ to carbonate is fast and proceeds through the formation of $Pb_3(CO_3)_2(OH)_2$ and $NaPb_2(CO_3)_2(OH)$; the conversion of $PbSO_4$ to $Pb_3(CO_3)_2(OH)_2$ occurs within 5 min [22]. On the other hand, the reaction of $Pb_2O(SO_4)$ is kinetically much slower, and lead oxides are practically inert in carbonate media. Table 7 provides a general indication of the reactions occurring.

Table 7 Reaction of lead sulphates in sodium carbonate media

Time (min)	$PbSO_4$	$Pb_2O(SO_4)$	$Pb_3(CO_3)_2(OH)_2$	$NaPb_2(CO_3)_2(OH)$
0	major	minor	—	—
5	—	minor	major	—
8	—	trace	major	trace
10	—	trace	major	minor
15	—	trace	major	major
30	—	faint trace	minor	major
60	—	—	trace	major
120	—	—	—	major

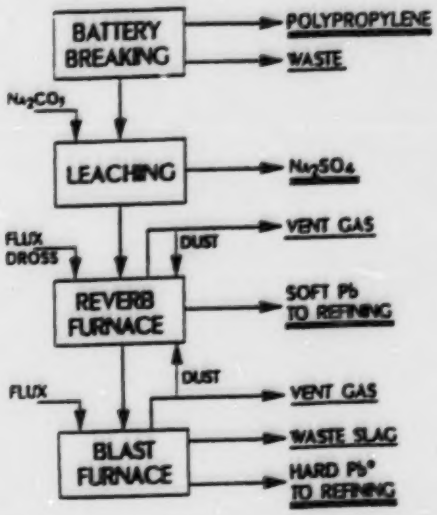

Fig.22 Schematic flowsheet of a smelting process based on Na_2CO_3 leached lead-acid battery paste

Detailed SEM-EDX studies of the lead-acid battery paste after various periods of reaction in Na_2CO_3 media confirmed the X-ray diffraction results presented in Table 7. In this regard, Figure 23 shows a large particle which initially consisted of $PbSO_4$ with inclusions of Pb metal. After a few minutes of reaction, the outer parts of the particle have been converted to $Pb3(CO3)2(OH)_2$, although a core of $PbSO_4$ remains. Significantly, there is no indication of any reaction of the Pb metal inclusions. Figure 24 shows the battery paste after 60 min of reaction. All the $PbSO_4$ has been converted, initially to $Pb_3(CO_3)_2(OH)_2$, and then to $NaPb_2(CO_3)_2(OH)$. Despite the extensive reaction of the sulphate phases, however, the bright-appearing mixture of PbO_2 and Pb_2O_3 remains unaltered.

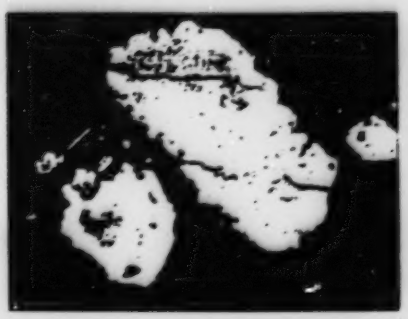

Fig.23 Backscattered electron micrograph of partly reacted $PbSO_4$ particles in the lead-acid battery paste. 1-$PbSO_4$, 2-$Pb_3(CO_3)_2(OH)_2$, 3-Pb

Fig.24 Backscattered electron micrograph of several extensively reacted particles in the battery paste. 1-$NaPb_2(CO_3)_2(OH)$, 2-PbO_2 + Pb_2O_3

Although the presence of PbO_2 and Pb_2O_3 creates problems for the electrolytic recovery of lead from the battery paste, the oxides do not pose a difficulty for the subsequent smelting of the product.

The data of Table 7 indicate the rapid reaction of $PbSO_4$ with sodium carbonate solutions. Accordingly, further studies on the $PbSO_4$-Na_2CO_3 reaction will not be rewarding with respect to commercial operations. A greater need is to elucidate the reaction of $Pb_2O(SO_4)$ with carbonate media and to develop improved technologies for the recovery of Na_2SO_4 from the spent leach solutions.

CONCLUSIONS

Metals recycling is a well established industry which is largely based on the use of pyrometallurgical techniques. Hydrometallurgical processes are being developed to leach Zn from galvanized scrap prior to remelting in an electric arc furnace (EAF), and a number of processes have been considered to leach Zn from EAF dusts. Because the EAF dusts are rich in halogens, chloride-based leaching systems may offer some advantages. Although the leach-solvent extraction-electrowinning process for copper has been highly developed, hydrometallurgy plays only a minor role in the recycling of copper scrap. Most copper scrap is melted, fire refined and cast into anodes. The hydrometallurgist does, however, play an important role in ensuring that the impurities present in the anodes do not contaminate the copper cathode deposit. Most lead is used to manufacture lead-acid batteries, and the recycling of spent batteries is a major industry. Hydrometallurgy plays an important role in the treatment of the paste component of the spent batteries, and that function could become more important if leach-electrowinning processes for lead-acid battery paste were implemented commercially. In this regard, the development of stable O_2-evolving anodes capable of working in fluoride-containing media is seen as a research priority.

Literature

[1] Hudson H.G. and Brandiff R.: U.S. Patent 3,905,882, September 1975.

[2] Dudek F.J., Daniels E.J. and Morgan W.A.: „Recycling galvanized steel: operating experience and benefits". World Zinc '93, I.G. Matthew, ed., Australas. Inst. Min. Metall., Parkville, Australia (1993), pp. 515-522.

[3] Houlachi G., Condy A. and Stanley R.W.: „Review of zinc recycling". Zinc & Lead '95, T. Azakami, N. Masuko, J.E. Dutrizac and E. Ozberk, eds., Mining & Materials Processing Inst. Japan, Tokyo, Japan (1995), pp.417-426.

[4] Zunkel A.D.: „EAF dust as an electrolytic zinc resource". Recycling of Metals and Engineered Materials, P.B. Queneau and R.D. Peterson, eds., Minerals, Metals & Materials Society, Warrendale, U.S.A. (1995), pp. 579-587.

[5] Anderson W.W., Opie W.R. and Rajcevic H.P.: „Caustic leach - electrowin zinc process pilot plant operation". Presented at the 110th Annual AIME Meeting, Chicago, U.S.A., February 1981.

[6] Nogueira E.D., Regife J.M. and Viegas M.P.: „Design features and operating experience of the Quimigal Zincex plant". Chloride Hydrometallury, P.D. Parker, ed., Metallurgical Society of AIME, Warrendale, U.S.A. (1982), pp. 59-79.

[7] Diaz G., Martin D. and Lombera C.: „Zinc recycling through the modified Zincex process". Recycling of Metals and Engineered Materials. P.B. Queneau and R.D. Peterson, eds., Minerals, Metals & Materials Society, Warrendale, U.S.A. (1995), pp. 623-635.

[8] Olper M.: „Zinc extraction from EAF dust with EZINEX process". Recycling of Metals and Engineered Materials. P.B. Queneau and R.D. Peterson, eds., Minerals, Metals & Materials Society, Warrendale, U.S.A. (1985), pp. 563-578.

[9] Olper M.: „The EZINEX process - a new and advanced way for electrowinning zinc from a chloride solution". World Zinc '93, I.G. Matthew, ed., Australas. Inst. Min. Metall., Parkville, Australia (1993), pp. 491-494.

[10] Genstskens R.: „Pressure leaching of zinc-bearing blast furnace dust". Lead-Zinc '90, T.S. Mackey and R.D. Prengaman, eds., Minerals, Metals & Materials Society, Warrendale, U.S.A. (1990), pp. 529-545.

[11] Van Weert G., van Sandwijk A., Kat W. and Honingh S.: „The treatment of iron making blast furnace dust by chloride hydrometallurgy". Hydrometallurgy Fundamentals, Technology and Innovation, J.B. Hiskey and G.W. Warren, eds., Society for Mining, Metallurgy and Exploration, Littleton, U.S.A. (1993), pp. 931-946.

[12] Van Sandwijk A. and Schipper-Zablotskaja M.: „Zinc oxide precipitation from solutions containing high concentrations of chloride ions". Hydrometallurgy Fundamentals, Technology and Innovation, J.B. Hiskey and G.W. Warren, eds., Society for Mining, Metallurgy and Exploration, Littleton, U.S.A. (1993), pp. 947-955.

[13] McElroy R.O. and Murray W.: „Developments in the Terra Gaia process for the treatment of EAF dust". Iron Control and Disposal, J.E. Dutrizac and G.B. Harris, eds., Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada (1996), pp. 505-517.

[14] Riveros P.A. and Dutrizac J.E.: „The precipitation of hematite from ferric chloride media". Hydrometallury, in press (1997).

[15] Chen T.T. and Dutrizac J.E.: „The mineralogy of copper electrorefining". JOM, 42 (1990) 39-44.

[16] Chen T.T. and Dutrizac J.E.: „Mineralogical characterization of anode slimes -IV Copper-nickel-antimony oxide („kupferglimmer") in CCR anodes and anode slimes". Can. Metall. Quart. 28 (1989) 127-134.

[17] Chen T.T. and Dutrizac J.E.: „A mineralogical study of the deportment and reaction of silver during copper electrorefining". Metal. Trans., 20B (1989) 345-361.

[18] Stout M.E.: „Secondary lead recovery from spent SLI batteries". Hydrometallury Fundamentals, Technology and Innovation, J.B. Hiskey and G.W. Warren, eds., Society for Mining, Metallurgy and Exploration, Littleton, U.S.A. (1993), pp. 1185-1195.

[19] Chen T.T. and Dutrizac J.E.: „The mineralogical characterization of lead-acid battery paste". Hydrometallury, 40 (1996) 223-245.

[20] Prengaman R.D.: „Recovering lead from batteries". JOM, 47 (1995) 31-33.

[21] Stout M.E.: „Secondary lead recovery from spent SLI batteries" EPD Congress 1993, J.P. Hager, ed., Minerals, Metals & Materials Society, Warrendale, U.S.A. (1992), pp. 967-979.

[22] Gong Y., Dutrizac J.E. and Chen T.T.: „The conversion of lead sulphate to lead carbonate in sodium carbonate media" Hydrometallurgy, 28 (1992) 399-421.

[23] Frias C., Garcia M.A. and Diaz G.: „Industrial size „PLACID" electrowinning cell" Aqueous Electrotechnologies: Progress in Theory and Practice, D.B. Dreisinger, ed., Minerals, Metals & Materials Society, Warrendale, U.S.A. (1996), pp. 101-113.

[24] Robinson D.J. and O'Keefe T.J.: „Studies relating to the development of an anode for lead electrowinning". Aqueous Electrotechnologies: Progress in Theory and Practice, D.B. Dreisinger, ed., Minerals, Metals & Materials Society, Warrendale, U.S.A. (1996), pp. 347.